(54) Title: EXPOSURE APPARATUS AND DEVICE MANUFACTURING METHOD
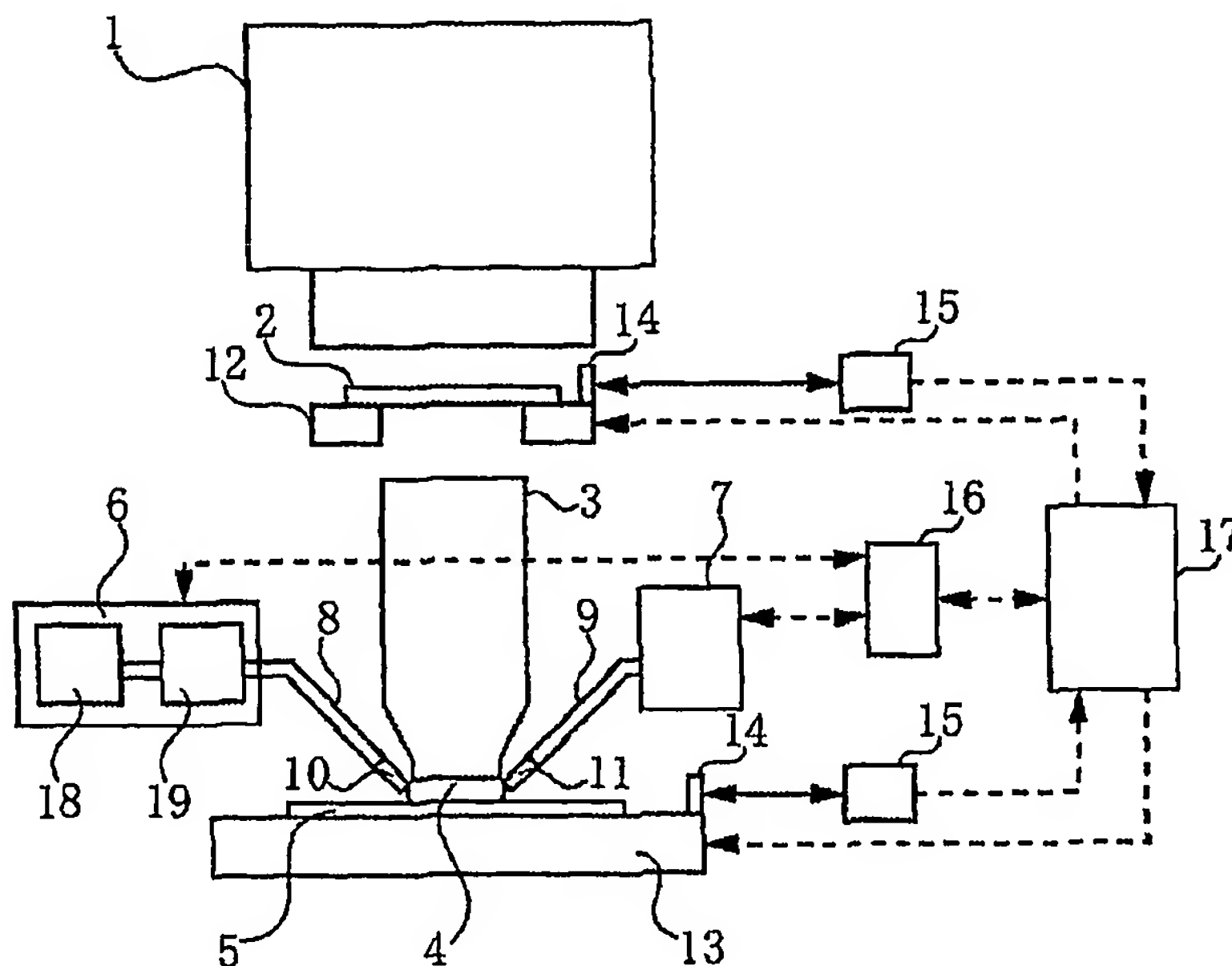
(57) Abstract: An exposure apparatus includes a projection optical system (3) for projecting a pattern of a mask (2) onto a substrate (5), and a fluid supply unit (6) for supplying a fluid between said projection optical system and the substrate, said fluid supply unit (6) including an injection unit (19) for injecting carbon dioxide into the fluid.

WO 2005/062351 A1

DESCRIPTION

EXPOSURE APPARATUS AND DEVICE MANUFACTURING METHOD

5   TECHNICAL FIELD

This invention relates generally to an exposure apparatus that utilizes an immersion method, and is suitable, for example, for the lithography process for
10   manufacturing highly integrated devices, such as semiconductor devices, e.g., ICs and LSIs, image pick-up devices, e.g., CCDs, display devices, e.g., a liquid crystal panels, communication devices, e.g., optical waveguides, and magnetic heads by transferring a
15   pattern of a mask (or a reticle) onto a photosensitive agent applied substrate.

BACKGROUND ART

20   An exposure apparatus for exposing a mask pattern onto a photosensitive-agent applied substrate have conventionally been used to manufacture semiconductor devices and liquid crystal panels. Since finer processing of a pattern is demanded for improved
25   integrations of devices, exposure apparatuses are improved so as to resolve fine patterns.

The following Rayleigh equation (1) defines
resolution R of a projection optical system in an
exposure apparatus, which is an index of a size of a
resolvable pattern:

5       $R = k_1 (\lambda / NA)$ (1)

where λ is an exposure wavelength, NA is a numerical
aperture of the projection optical system at its image
side, and k_1 is a constant determined by a development
process and others, which usually is approximately 0.5.

10   As understood from Equation (1), the resolving
power of the optical system in the exposure apparatus
becomes higher as the exposure wavelength is shorter
and the image-side NA of the projection optical system
is greater.

15   Therefore, following the mercury lamp i-line (with
approximately 365 nm in wavelength), a KrF excimer
laser (with approximately 248 nm in wavelength) and an
ArF excimer laser (with approximately 193 nm in
wavelength) have been developed, and more recently an

20   F_2 excimer laser (with approximately 157 nm in
wavelength) is reduced to practice. However, a
selection of the exposure light having a shorter
wavelength makes it difficult to meet material
requirements with respect to transmittance, uniformity

25   and durability, etc., causing an increasing cost of the
apparatus.

An exposure apparatus having a projection optical
system with a NA of 0.85 is commercially available, and
a projection optical system with a NA of 0.9 or greater
is researched and developed. Such a high-NA exposure
5   apparatus has difficulties in maintaining good imaging
performance with little aberration over a large area,
and thus utilizes a scanning exposure system that
synchronizes the mask with a substrate during exposure.

However, a conventional design cannot make the NA
10   greater than 1 in principle due to a gas layer having a
refractive index of about 1 between the projection
optical system and the substrate.

On the other hand, an immersion method is proposed
as means for improving the resolving power by
15   equivalently shortening the exposure wavelength. It is
a method used for the projection exposure, which fills
liquid in a space between the final surface of the
projection optical system and the substrate, instead of
filling this space with air as in the prior art. The
20   projection exposure apparatus uses, as the immersion
method, a method for immersing the final surface of the
projection optical system and the entire substrate in
the liquid tank (see, for example, Japanese Patent
Application, Publication No. 6-124873), and a local
25   fill method that flows the fluid only in the space
between the projection optical system and the substrate

(see, for example, International Publication No. WO99/49504 pamphlet).

The immersion method has an advantage in that the equivalent exposure wavelength has a wavelength of a

5 light source times 1 / n, where n is a refractive index of the used liquid. This means that the resolving power enhances by 1 / n times the conventional resolving power, even when the light source having the same wavelength is used.

10 For example, when the light source has a wavelength of 193 nm and the fluid is the water, the refractive index is about 1.44. Therefore, use of the immersion method can improve the resolving power by 1 / 1.44 times the conventional method.

15 The most common fluid used for the immersion method is water. The water has a good transmittance relative to the ultraviolet light down to about 190 nm. In addition, advantageously, a large amount of water is used in the semiconductor manufacturing process, and

20 the water gets along with the wafer and photosensitive agent.

It is important to reduce the influence of the air gas bubbles to the exposure in the immersion exposure apparatus. These gas bubbles that enter the exposure

25 area between the final surface of the projection optical system and the substrate scatter the exposure light. Therefore, the transferred pattern's critical

dimension varies beyond the permissible range, causing

insulations and short circuits contrary to the design

intent in the worst case. Degassing of the fluid is

the most effective, known method to prevent the

5 influence of the gas bubbles to the exposure. Since

the gas bubbles are unlikely to occur or the generated

gas bubbles extinguish in a short time period in the

degassed fluid, the influence of the gas bubbles to the

exposure is prevented.

10   However, the water widely used for the immersion

method increases the resistivity, when degassed, and is

likely to generate static electricity disadvantageously.

For example, the pure water (*i.e.*, the water containing

few impurities) used for the semiconductor

15 manufacturing process reaches the resistivity of 18

$M\Omega \cdot cm$ after degas. The substrate surface is

electrically insulated since the photosensitive agent

is applied on it. Therefore, as the stage moves the

substrate, the static electricity is generated on the

20 substrate surface and makes the device on the substrate

defective.

DISCLOSURE OF INVENTION

25   With the foregoing in mind, the present invention

has an exemplary object to provide an exposure

apparatus that uses an immersion method while reducing
the static electricity on the substrate.

An exposure apparatus according to one aspect of
the present invention includes a projection optical
5   system for projecting a pattern of a mask onto a
substrate, and a fluid supply unit for supplying a
fluid between the projection optical system and the
substrate, the fluid supply unit including an injection
unit for injecting carbon dioxide into the fluid.

10   An exposure apparatus according to another aspect
of the present invention includes an illumination
optical system for illuminating a mask using light from
a light source, and a projection optical system for
projecting a pattern of the mask onto a substrate,

15   wherein a fluid supplied to a space between the
projection optical system and the substrate has a
concentration of carbon dioxide between 0.02 ppm and
750 ppm.

An exposure apparatus according to still another
20   aspect of the present invention includes an
illumination optical system for illuminating a mask
using light from a light source, and a projection
optical system for projecting a pattern of the mask
onto a substrate, wherein a fluid supplied to a space
25   between the projection optical system and the substrate
has a resistivity value between 0.02 MΩ·cm and 10 MΩ·cm.

A device manufacturing method according to another aspect of the present invention includes the steps of exposing an object using the above exposure apparatus, and developing the exposed object.

5   Other objects and further features of the present invention will become readily apparent from the following description of the embodiments with reference to accompanying drawings.

10   **BRIEF DESCRIPTION OF DRAWINGS**

The accompanying drawings, which are incorporated in and constitute a part of the specification, illustrate embodiments of the invention and, together with the description, serve to explain the principles of the invention.

FIG. 1 is a schematic view of a principal part in an exposure apparatus of a first embodiment.

FIG. 2 is a schematic view showing a structural example of an injection unit of carbon dioxide.

FIG. 3 is an explanatory view showing a relationship between a potential on a wafer and a pure water's resistivity in a wafer's cleansing step.

FIG. 4 is an explanatory view showing a relationship between the pure water's resistivity and the concentration of carbon dioxide.

FIG. 5 is an explanatory view showing a relationship between a normalized life of a gas bubble and a normalized concentration of a dissolved gas.

FIG. 6 is an explanatory view showing a relationship between a water's PH value and a concentration of the carbon dioxide.

FIG. 7 is a schematic view showing a principal part of an exposure apparatus as a variation of the first embodiment.

FIG. 8 is a manufacture flow of a device.

FIG. 9 is a wafer process shown in FIG. 8.

BEST MODE FOR CARRYING OUT THE INVENTION

Preferred embodiments of the present invention will now be described in detail in accordance with the accompanying drawings.

FIRST EMBODIMENT

FIG. 1 is a schematic view of a principal part of an exposure according to a first embodiment. This embodiment applies the present invention to a scanning exposure apparatus.

In FIG. 1, 1 denotes an illumination optical system for illuminating a reticle (or a mask) with light from a light source. The light source is an ArF excimer laser (with a wavelength of 193 nm), a KrF

excimer laser (with a wavelength of 248 nm), and F_2 laser, and the illumination optical system 1 includes a known optical system etc. (not shown). 3 denotes a refracting or catadioptric or another projection

5   optical system for projecting a circuit pattern of a reticle 2 illuminated by the illumination optical system 1, onto a wafer 5 (substrate) as a second object. 15 denotes a distance measuring laser interferometer for measuring a two-dimensional position on a

10   horizontal plane of each of a reticle stage 12 and a wafer stage 13 via a reference mirror 14. A stage controller 17 controls positioning and synchronizations of the reticle 2 and the wafer 5 based on this measurement value. The wafer stage 13 serves to adjust

15   a position in a longitudinal direction, a rotational angle, and an inclination of a wafer so that the surface of the wafer 5 matches the image surface of the projection optical system 3.

　　　This embodiment uses the immersion method to

20   shorten the equivalent exposure wavelength, and improve the exposure resolution. Therefore, this embodiment arranges a supply port 10 and a recovery port 11 around the final surface of the projection optical system 3, supply the water between the final surface of the

25   projection optical system 3 and the wafer 5, and form a liquid film 4 there. An interval between the final surface of the projection optical system 3 and the

wafer 5 is preferably small enough to stably form the

liquid film 4, such as 0.5 mm. The supply port 10 is

connected via a supply tube 8 to a fluid supply unit 6

that supplies the water. The recovery port 11 is

5   connected via a recovery tube 9 to a fluid recovery

unit 7 that recovers the water. The fluid supply unit

6 includes a degassing unit 18 and a carbon dioxide

injection unit 19 provided at the downstream of the

degassing unit 18. The degassing unit 18 can have, for

10   example, a well-known membrane module (not shown) and a

vacuum pump (not shown). An immersion controller 16

sends a control signal to the fluid supply unit 6 and

the fluid recovery unit 7, and transmits and receives

data with a stage controller 17. Thereby, the

15   immersion controller 16 adjusts the liquid supply

amount and recovery amount according to the wafer's

moving direction and speed.

This embodiment injects a predetermined

concentration of carbon dioxide into the degassed water,

20   prevents influence of gas bubbles to the exposure, and

restrains the static electricity on the substrate.

Carbon dioxide advantageously is inexpensive and does

not contaminate the substrate. Referring to FIG. 2, a

description will be given of one exemplary structure of

25   the carbon dioxide injection unit 19. A membrane

module 22 is provided between an inflow port 20 of the

water and an outflow port 21. The membrane module 22

is connected to a supply source 24, such as a CO_2 cylinder, via a valve 23. The valve 23 is electrically controlled by a carbon dioxide controller 25.

This configuration restrains a concentration of
5   the carbon dioxide in the water by changing the flow of the carbon dioxide to the membrane module 22 via the valve 23. A resistivity meter 26 is provided at a downstream side of the carbon dioxide injection unit. It is more preferable to control the concentration of
10 the carbon dioxide within a predetermined range by electrically feeding back an output of the resistivity meter 26 to the carbon dioxide controller 25. Carbon dioxide gas may be injected into the water from a nozzle instead of using a membrane module. In this
15 case, it is preferable to eliminate fine particles in the carbon dioxide gas using a filter in advance.

A description will now be given of an optimal concentration of carbon dioxide.

The lower limit of the carbon-dioxide
20 concentration is determined from the necessity to restrain the static electricity on the wafer. FIG. 3 shows a relationship between the potential on the wafer and the water's resistivity when the wafer is cleansed with pure water from the nozzle (as detailed in Asano,
25 "Spray, Contact, Flow Charges of Pure Water and Ultra-pure Water", The Institute of Electrical Engineering of Japan, Vol. 108 (1988), pp. 362-366). It is understood

from FIG. 3 that when the water's resistivity exceeds
10 MΩ·cm, the large potential is likely to generate on
the wafer. On the other hand, when the water's
resistivity is equal to or smaller than 5 MΩ·cm, the

5   static electricity does not pose a problem. FIG. 4
shows a relationship between the carbon-dioxide
concentration and the resistivity in the pure water.
As the carbon-dioxide concentration increases, the
resistivity decreases. The carbon-dioxide

10   concentrations of 0.02 ppm and 0.06 ppm correspond to
the resistivity of 10 MΩ·cm and 5 MΩ·cm. This means
that the carbon-dioxide concentration in the water is
preferably 0.02 ppm or greater, more preferably 0.06
ppm or greater, in order to restrain the static

15   electricity on the wafer.

The upper limit of the carbon-dioxide
concentration can be determined from a problem of the
gas bubbles. The gas-bubble generation is caused by a
pressure variance in the water and inclusions of fine

20   gas bubbles in the carbon-dioxide injection unit. In
either case, as the carbon-dioxide concentration in the
water increases, the gas bubble is likely to generate
and its life (or a time period during which a generated
gas bubble extinguishes due to diffusion) becomes long.

25   In other words, the gas bubble is unlikely to
extinguish and a danger of the influence of the gas
bubbles to the exposure increases. FIG. 5 shows the

normalized life τ / τ_0 of a gas bubble as a function of C_s / C_∞ as a normalized concentration of dissolved gas (as detailed in C. E. Brennen, "Cavitation and Bubble Dynamics, "Oxford University Press (1995), Chapter 2).

5 Here, τ_0 is the life when $C_\infty = 0.0$ and Cs is a saturated concentration. When normalized concentration C_s / C_∞ is 0.2 or smaller, the life of a gas bubble is close to $C_\infty = 0.0$ and the gas bubble is likely to extinguish relatively immediately. On the other hand, when

10 normalized concentration C_s/C_∞ becomes 0.5 or greater, the life of a gas bubble drastically increases and gas bubble is unlikely to extinguish. As a result of this, in order to prevent the influence of the gas bubble to the exposure, the concentration of gas dissolved in the

15 water is preferably 50 % or smaller of the saturated concentration, and more preferably 20 % or smaller of the saturated concentration. The saturated concentration of carbon dioxide in the water is about 1500 ppm in one air pressure. Therefore, in order to

20 prevent the influence of the gas bubbles to the exposure, the carbon-dioxide concentration may be preferably 750 ppm or smaller, more preferably 300 ppm. These values are much greater than the lower limit of the carbon-dioxide concentration necessary to restrain

25 the static electricity, and it is possible to reconcile the prevention of the gas bubble's influence with the restraint of the static electricity.

In summary, the carbon-dioxide concentration in the water supplied to the liquid film 4 ranges preferably from 0.02 ppm to 750 ppm, and more preferably from 0.06 ppm to 300 ppm. The equivalent
5   condition is that the resistivity ranges preferably from 0.02 M$\Omega \cdot$cm to 10 M$\Omega \cdot$cm, and more preferably from 0.04 M$\Omega \cdot$cm to 5 M$\Omega \cdot$cm. This configuration prevents the influence of the gas bubbles to the exposure and restrains the static electricity on the substrate.